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First-Principles Simulation of Intrinsic Collision Cascades in KCl and NaCl to Test Interatomic Potentials at Energies between 5 and 350 eV

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Theoretical interatomic potentials for KCl and NaCl are tested at energies 5–350 eV against experimental data from intrinsic collision cascades. The collisional scattering of Cl with Cl, K, and Na atoms was observed from Doppler-shifted γ rays depopulating an excited state in recoiling ^{36}Cl produced through the thermal neutron capture $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl}$. The collisional scattering was simulated with molecular dynamics. Interatomic potentials from the present *ab initio* atomic cluster calculations are proposed for the Cl-Cl, Cl-K, and Cl-Na interactions in KCl and NaCl.

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The description of the interaction between colliding atoms in condensed matter is one of the classic problems of atomic and solid-state physics. In the energy range below 1 keV, the pairwise potential is determined by the interplay between (i) nuclear Coulomb repulsion (screened by atomic electrons), (ii) the kinetic (Pauli) repulsion arising from the overlapping electron states, and (iii) the exchange and correlation amongst the electrons. A broad spectrum of approximate interatomic potentials have been reported in the literature [1].

The interatomic potentials calculated from overlapping rigid atomic (e.g., Hartree-Fock) charge distributions and using first-order perturbation theory and a local-density approximation have been evaluated in several studies [1]. The results of different calculations show large scatter between interatomic potentials at radial separation distances larger than 0.5 Å. With this in mind, Ziegler, Biersack, and Littmark [1] (ZBL) suggested an empirically determined universal interatomic screening function and hence a universal interatomic potential, which is widely used in various contexts. The deficiencies of this repulsive potential at low energies are apparent for accurate applications in individual cases and crystalline materials. A related approach to interatomic potentials was suggested by Gordon and Kim [2,3] (GK). They showed that bond strengths, bond distances, and vibrational frequencies of alkali halide molecules can be reproduced by a simple local-density approach. The validity of this potential energy is questionable at distances shorter than 2 Å. Advances in computational techniques have now made it feasible to attack the problem of interatomic potentials without resorting to the approximation of overlapping atoms [4].

From an experimental point of view, the interatomic potential can be deduced from crystal data [5] such as phonon dispersion curves, elastic constants, compressibility, and lattice constants. For small nuclear separations where this method cannot be used, the repulsive part of

the interatomic potential has been studied by measuring cross sections for ion-atom collisions [1]. The shortcoming of this method is that the scattering takes place at a crystal surface or in a gas, i.e., not in bulk matter, and that energies of the order of 10–1000 eV cannot be probed reliably. The very recently developed γ -ray-induced Doppler-broadening (GRID) method [6] allows one to experimentally test interatomic potentials in this energy region in bulk matter [7].

In this Letter we use first-principles simulations of collision cascades in bulk alkali halides KCl and NaCl to test interatomic potentials for the Cl-Cl, Cl-K, and Cl-Na interactions at distances 0.6–1.8 Å, i.e., at potential energies 350–5 eV, respectively. We use a novel procedure, where (i) measurements of a Doppler-broadened γ -ray line shape produced by ^{36}Cl nuclei in Cl atoms recoiling at energies below 700 eV after the thermal neutron capture reaction $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl}$ and emission of primary γ rays, (ii) the independently determined mean lifetime value of the excited nuclear state emitting the γ rays under study, (iii) full molecular dynamics (MD) simulations of intrinsic collision cascades, and (iv) the simulation of the γ -ray line shape are combined to test the ZBL and GK potentials and the potentials obtained in *ab initio* atomic cluster (AC) calculations.

The measurements of the intrinsic collision cascades with the GRID method were performed at the Institute Laue-Langevin (ILL) high flux reactor with the two-axis flat-crystal spectrometer GAMS4 [8,9]. Details of the measurements have been given in a recent paper [10].

Recoiling ^{36}Cl atoms for atom-ion scattering in bulk KCl and NaCl were produced in the thermal neutron capture reaction $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl}$ [10]. The initial recoil velocity 5.92×10^4 m/s was imparted to the ^{36}Cl atom by a primary 6.62-MeV γ -ray transition populating the $E_x = 1.959$ MeV state. The information on the collisional scattering was obtained from the Doppler shift of the secondary 1959-keV γ ray. The observable Doppler shift

depends on the velocity of ^{36}Cl and the angle between the recoil direction and the direction of the 1959-keV γ ray. The isotropic emission of primary γ rays yields the Doppler-broadened line shape for the 1959-keV γ rays which reflects the interplay between the lifetime of the 1.959-MeV state and the slowing-down time (governed by the interaction potentials Cl-Cl, Cl-K, and Cl-Na) of the recoiling ^{36}Cl in KCl and NaCl. The measured 1959-keV line shape in the KCl target is shown in Fig. 1.

In the MD simulations the equations of motion of both the recoiling and target atoms were integrated numerically [11] with a time step of 0.5 fs. The MD cell comprised 216 atoms with periodic boundary conditions applied in all three dimensions. Atoms were initially placed in fcc arrays with velocities to yield the temperatures valid during experiment, i.e., 607 ± 14 K for KCl and 840 ± 40 K for NaCl. The temperatures were obtained by determining the Maxwellian velocity distribution of thermalized ^{36}Cl atoms from the broadening of the 788-keV γ -ray line shape, corresponding to the decay of the long-living ($\tau = 19.9$ ps, Ref. [12]) 0.788-MeV state. Before initiating the collision cascade, the lattice was thermally equilibrated for 160 time steps of 5 fs. The accumulation of the recoil energy in the MD cell during the simulation of a collision cascade was prevented by scaling the velocities of the atoms other than the recoiling atom in such a way that the temperature of the cell was initialized every 30 fs. This is the minimum time a recoiling ^{36}Cl atom needs to travel through the MD cell used and was obtained to be the longest time step not affecting the final results. The reason behind the fact that the temperature scaling corrected the lifetime values (see below) by only a factor

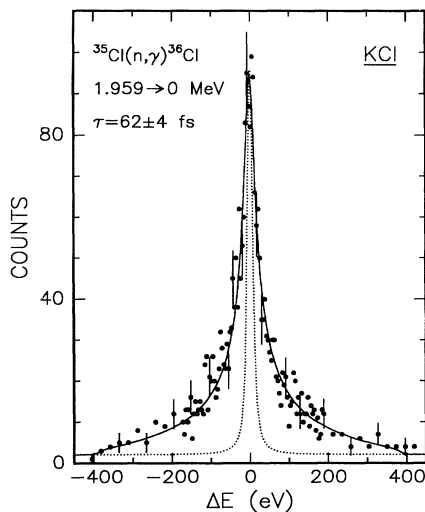


FIG. 1. Experimental (circles) and simulated (solid line) γ -ray line shape for the 1959-keV transition produced in the neutron capture reaction in KCl target. The atomic cluster (AC) potential and the lifetime value of 62 fs for the 1.959-MeV state in ^{36}Cl were used in the simulation. The dotted line is the instrumental response function of the spectrometer.

of 0.94 is that about 76% of the recoiling ^{36}Cl atoms did not cross the boundary of the MD cell, 20% crossed it once, and 4% crossed it twice or more before the emission of the γ ray under study. Details of the simulation techniques are reported elsewhere [13,14].

In addition to the direct decay, the capture state decays to the 1.959-MeV state via intermediate states [15]. In these cases the recoil velocity is imparted to the ^{36}Cl atom in several steps. The effect of these cascade γ rays on the velocity vector of ^{36}Cl was taken into account. In the simulations of the experimental γ -ray line shapes, different decay branches were weighted by the branching ratios taken from Ref. [15].

The test of the potentials which describe the Cl-Cl, Cl-K, and Cl-Na interactions and govern the slowing-down time of the recoiling Cl atoms requires an accurate and reliable lifetime value of the 1.959-MeV state. Such a value was measured through the reaction $^{36}\text{S}(p,n)^{36}\text{Cl}$ at $E_p = 4.150$ MeV using the improved Doppler-shift attenuation (DSA) method, e.g., Ref. [16] and references therein. A ^{36}S target implanted into Ta was used in the measurements. The DSA measurements to be reported in detail elsewhere [14] are illustrated in Fig. 2.

The relevant data needed in the DSA analysis for description of the slowing down of the recoiling 110-keV ^{36}Cl atoms in Ta are available from a recent study [17]. In the stopping power described by

$$\left(\frac{dE}{dx} \right)_{\text{corr}} = f_n \left(\frac{dE}{dx} \right)_n + f_e \left(\frac{dE}{dx} \right)_e, \quad (1)$$

the uncorrected nuclear stopping power $(dE/dx)_n$ was calculated by deriving the scattering angles of the recoiling atoms directly from the classical scattering integral

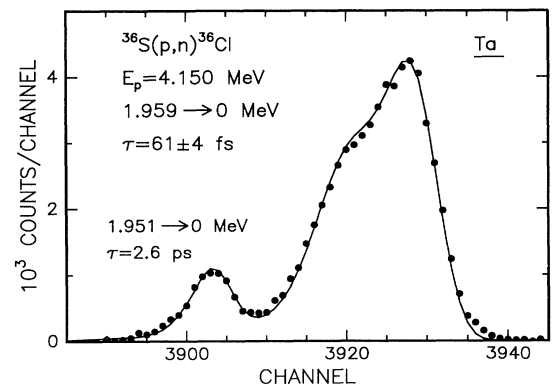


FIG. 2. Portion of γ -ray spectrum recorded in the DSA measurements of the 1.959-MeV ^{36}Cl state. The solid line is the computer simulation of the γ -ray line shape observed at 0° relative to the beam direction. The fit is shown for the lifetime 61 fs. Also shown is the γ -ray peak from the 1951-keV transition. The computer simulation of the 1951-keV line shape was done with the lifetime value $\tau(1.951 \text{ MeV}) = 2.6$ ps taken from Ref. [12].

and universal potential of Ziegler, Biersack, and Littmark [1] which is expected to be valid in the keV-energy region. The uncorrected electronic stopping power $(dE/dx)_e$ was taken from the semiempirical theory [1]. The binary collision approximation (BCA) simulation of the stopping data [17] with the inclusion of the polycrystalline structure of Ta resulted in the values of 1.00 ± 0.05 and 1.35 ± 0.16 for the correction factors f_n and f_e , respectively.

The BCA simulation of the 1959-keV γ -ray line shape (Fig. 2) gives a lifetime value of 61 ± 4 fs for the 1.959-MeV state. The uncertainty of the lifetime is mainly due to the uncertainty of the experimentally determined stopping power; the statistical uncertainty is 1.2 fs.

Three interatomic potentials shown in Fig. 3, were used in the simulation of the GRID data. The Gordon-Kim potential [2,3] has been obtained by calculating the energy change of the overlapping electron distributions using a local-density approximation for electron exchange, correlation, and the kinetic energy. The GK potential was taken to be the short-range version reported in Ref. [3]. The universal potential (ZBL) has been derived by Ziegler, Biersack, and Littmark [1] by fitting a universal screening function to the results of calculations similar to those of Gordon and Kim. The ZBL potential was calculated using the universal ZBL screening function [1] for neutral atoms. In order to obtain the right lattice positions in the simulations with the GK and ZBL potentials, the Coulombic term due to ionic charges was included for the interaction between lattice atoms.

A novel potential given in Table I was obtained from

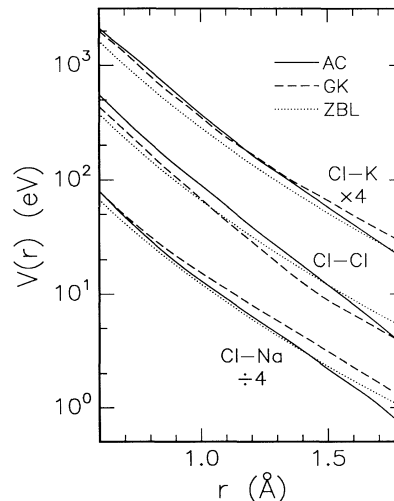


FIG. 3. Pair potentials for Cl-Cl, Cl-K, and Cl-Na used in the simulations of GRID data illustrated in Fig. 1. In the figure the Cl-K potentials have been multiplied by 4 and the Cl-Na potentials divided by 4.

atomic cluster calculations. The potential was calculated using the Kohn-Sham density-functional theory, with a local-density formula for electron exchange and correlation, for a cluster of atoms in a prescribed geometry. The density-functional equations were solved using the discrete-variational method with numerical atomic basis functions [18,19]. The Cl-Cl, Na-Cl, and K-Cl pair potentials were determined by calculating the total energy

TABLE I. Interatomic AC potentials used in the simulations of GRID data.

Interatomic separation (Å)	Potential energy (eV) ^a		
	Cl-Cl ⁻	Cl-K ⁺	Cl-Na ⁺
0.4	1.461(3)	1.568(3)	9.990(2)
0.6	5.542(2)	5.329(2)	3.144(2)
0.8	2.100(2)	2.255(2)	1.161(2)
1.0	9.059(1)	9.381(1)	5.170(1)
1.2	3.909(1)	4.187(1)	2.588(1)
1.4	1.790(1)	2.071(1)	1.284(1)
1.6	8.161	1.026(1)	6.155
1.8	3.482	5.107	2.762
2.0	1.141	2.511	1.052
2.2	2.923(-2)	1.222	1.491(-1)
2.4	-4.207(-1)	4.755(-1)	-2.239(-1)
2.6	-5.328(-1)	4.734(-2)	-3.470(-1)
2.8	-4.894(-1)	-1.561(-1)	-3.628(-1)
3.0	-3.880(-1)	-2.248(-1)	-3.213(-1)
3.2	-2.771(-1)	-2.284(-1)	-2.604(-1)
3.4	-1.785(-1)	-2.015(-1)	-2.156(-1)
3.6	-9.951(-2)	-1.674(-1)	-7.346(-2)
3.8	-4.081(-2)	-1.333(-1)	0.000
4.0	0.000	-4.554(-2)	0.000

^aThe notation (*n*) means $\times 10^n$.

of a negative Cl_2^- and positive NaCl^+ and KCl^+ dimers as a function of the bond distance. The charges of the dimers were chosen in order to describe the interactions of a recoiling neutral Cl atom with the ions of the alkali halide crystal. The net charge of dimers does not have a significant effect on the potential in the energy region of interest. The potentials calculated for neutral NaCl and KCl dimers were in good agreement with the GK potential including the Coulombic term in the region of the attractive potential.

The potentials for the recoiling Cl atom were truncated at interatomic separations of 4.0 Å in KCl and 3.6 Å in NaCl.

The best fits of the simulated line shapes to the experimental 1959-keV line shapes resulted in the lifetime values of 63 ± 4 fs (GK), 66 ± 4 fs (ZBL), and 62 ± 4 fs (AC) for KCl, and 61 ± 5 fs (GK), 65 ± 5 fs (ZBL), and 62 ± 5 fs (AC) for NaCl. The experimental uncertainties, i.e., those of the temperature and instrumental resolution, are negligible compared to the statistical uncertainty and the uncertainty of 2 fs due to uncertainties of the feeding intensities and lifetime values.

The lifetime values obtained with all the potentials are systematically somewhat longer than the standard value of 61 ± 4 fs but within the 1σ error limits in agreement with it. However, by comparing the potentials illustrated in Fig. 3, we see that for the Cl-Cl interaction, the AC potential is about 20% more repulsive than the GK potential and ZBL potential at distances shorter than about 1.2 Å. For the Cl-K interaction, the AC potential is close to the GK potential but is about 20% more repulsive than the ZBL potential. For the Cl-Na interaction, the AC potential is not in disagreement with the ZBL potential but from 0.6 to 1.8 Å is between 0% and 30%, respectively, less repulsive than the GK potential. Therefore, in spite of the remarkable differences between the potentials similar slowing-down times for Cl atoms in KCl and NaCl are obtained as total effects. The AC potential should be preferred, as it is based on a minimum number of approximations and contains no adjustable parameters.

In conclusion, first experimental information on the interatomic potentials of Cl-Cl, Cl-K, and Cl-Na interactions in alkali halides KCl and NaCl was obtained in the energy range 5–350 eV. The measured Doppler-broadened line shapes of the 1959-keV γ rays emitted from the 1.959-MeV nuclear state of recoiling ^{36}Cl , whose lifetime was determined independently, were compared with the line shapes simulated by using the MD calculations for the description of intrinsic collision cascades. Within the experimental uncertainties, the line

shapes corresponding to the standard lifetime and reflecting the relation between the lifetime and the slowing-down times of the recoiling ^{36}Cl atoms in KCl and NaCl were reproduced by the Gordon-Kim [2,3] (GK), universal [1] (ZBL), and present *ab initio* atomic cluster (AC) potentials. The results show, however, that if one potential is chosen for one interaction, the other potentials cannot be used anymore to describe the other interactions.

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